

# On the anomalous thermal evolution of the low-temperature, normal-state specific heat of various nonmagnetic intermetallic compounds.

M. ElMassalami

*Instituto de Física, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, Brazil*  
(Dated: November 15, 2011)

## Abstract

The low-temperature normal-state specific heat and resistivity curves of various nonmagnetic intermetallic compounds manifest an anomalous thermal evolution. Such an anomaly is exhibited as a break in the slope of the linearized  $C/T$  versus  $T^2$  curve and as a drop in the  $R$  versus  $T$  curve, both at the same  $T_{\beta\gamma}$ . It is related, not to a thermodynamic phase transition, but to a Kohn-type anomaly in the density of states curves of the phonon or electron subsystems. On representing these two anomalies as additional Dirac-type delta functions, situated respectively at  $k_B\theta_L$  and  $k_B\theta_E$ , an analytical expression for the total specific heat can be obtained. A least-square fit of this expression to experimental specific heat curves of various compounds reproduced satisfactorily all the features of the anomalous thermal evolution. The obtained fit parameters (in particular the Sommerfeld constant  $\gamma_0$  and Debye temperatures  $\theta_D$ ) compare favorably with the reported values. Furthermore, the analysis shows that (i)  $T_{\beta\gamma}/\theta_L = 0.2 (1 \pm 1/\sqrt{6})$  and (ii)  $\gamma_0 \propto \theta_D^{-2}$ ; both relations are in reasonable agreement with the experiments. Finally, our analysis (based on the above arguments) justifies the often-used analysis that treats the above anomaly in terms of either a thermal variation of  $\theta_D$  or an additional Einstein mode.

PACS numbers: 74.25.Bt; 65.40.Ba ; 63.20.kd

## I. INTRODUCTION

The low-temperature, normal-state specific heat of a nonmagnetic intermetallic is usually described in term of a sum of lattice,  $C_L$ , and electronic,  $C_E$ , contributions.<sup>1</sup> The former is commonly approximated by the Debye model ( $C_L = \beta T^3$  for  $T \ll \theta_D$ ;  $\theta_D$  is the Debye temperature) while the latter by the Sommerfeld model ( $C_E = \gamma T$  for  $T \ll \theta_F$ ;  $\theta_F$  is the Fermi temperature). Considering that at liquid helium temperatures these two inequalities are strictly satisfied, then any simultaneous changes in  $\beta$  and  $\gamma$  would signal a related variation in the spectral features of the phonon or electron subsystem. Surprisingly, this very  $\beta\gamma$ -change is evident as a break in the slope of the normal-state  $C/T$  versus  $T^2$  curve, a break that separates two distinct linearized sections; these linearly extrapolated upper and lower sections intersect at  $T_{\beta\gamma}$  which is taken to be a measure of the energy of this event.

Varieties of materials exhibit this  $\beta\gamma$ -change: examples include group V transition metals V, Nb and Ta (Fig. 1)<sup>2-5</sup> the Chevrel phases  $\text{PbMo}_6\text{X}_8$  ( $\text{X}=\text{S}, \text{Se}$ ),<sup>6,7</sup> the A12-type  $\text{Re}_3\text{W}$ ,<sup>8</sup> the A15-type  $\text{Nb}_3\text{Sn}$  and  $\text{V}_3\text{Si}$  (Fig. 2),<sup>9,10</sup> the layered  $\text{NbSe}_2$ ,<sup>11</sup> the perovskite  $\text{MgCNi}_3$  (Fig. 3),<sup>12</sup> the borocarbides  $\text{RNi}_2\text{B}_2\text{C}$  ( $R=\text{Y}, \text{La}, \text{Lu}$ ) (Fig. 4),<sup>13-16</sup>  $\text{Li}_2(\text{Pd}_{1-x}\text{Pt}_x)_3\text{B}$  ( $x=0, 0.5, 1$ ) (Fig. 5),<sup>17</sup> and  $\text{Li}_x\text{RhB}_{1.5}$  ( $x=0.8, 1.0, 1.2$ ).<sup>18</sup> In particular, for  $\text{Nb}_3\text{Sn}$ , this  $\beta\gamma$ -change was shown to be required by the condition of entropy balance.<sup>9,10</sup>

Generally, the analysis of the normal-state specific heat is undertaken so as to obtain  $\theta_D$  from  $\beta$  and  $N(E_F)$  from  $\gamma$  [ $N(E_F)$  is the density of states at the Fermi level,  $E_F$ ], then it is not surprising that such a  $\beta\gamma$ -anomaly did not attract much attention; rather it is considered as an undesirable complication that hinders the precise evaluation of  $\theta_D$  and  $N(E_F)$ . In spite of this back-

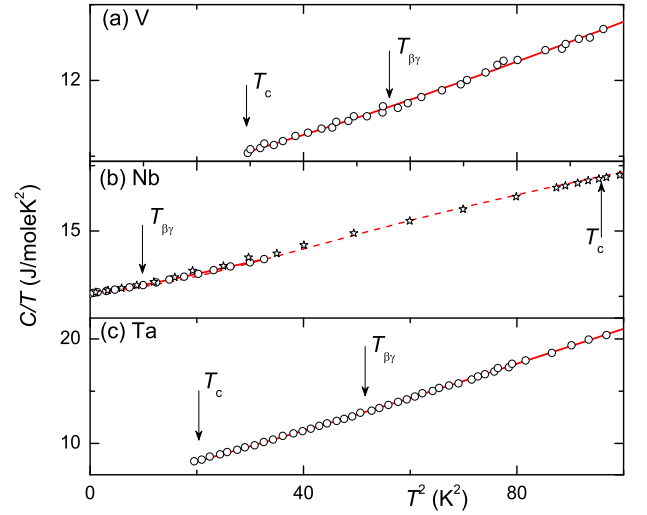


FIG. 1:  $C/T$  versus  $T^2$  curves of (a) V,<sup>5</sup> (b) Nb ( $H = 1.15$  T),<sup>4,5</sup> (c) Ta.<sup>5</sup> Lines are fits to Eq. 8 with parameters as given in Table I. For (b) the solid line is a fit to the data (circles) of Da Silva *et al.*<sup>4</sup> while the dashed line to those (stars) of Leupold *et al.*<sup>5</sup>

ground, some dedicated investigations were carried out even though no common agreements on the interpretation were reached.<sup>2-5,9,10,19,20</sup> Nevertheless, there was a consensus about the following common features.

First, the manifestation of a  $\beta\gamma$ -change is evident in various compounds such as normal intermetallics as well as the normal-state of type II superconductors: each compound differs strongly from the others in its crystal structure, chemical composition, electronic properties, and the type of superconductivity (whether conventional or unconventional). As a result, there are strong differences in  $T_{\beta\gamma}$ , in the strength of the event, and in

TABLE I: Normal-state parameters of various compounds as obtained from the least-squares fit of Eq. 8 to the data of Figs. 1-5.  $T_c$  is the superconducting critical temperature at zero field; *sc* (*pc*) denotes a single-crystal (polycrystalline) sample. Other symbols are explained in the text.

Compound	$T_c$ K	$T_{\beta\gamma}$ K	$\theta_D$ K	$\theta_L$ K	$\gamma_0$ mJ/mol K <sup>2</sup>	b	$T_{\beta\gamma}/\theta_L$	Ref
Nb	9.28	3.11	275	31.3	7.8	0.0017	0.099	4,5
V	5.4	7.5	397	76.0	9.7	0.0056	0.099	5,11
Ta	4.5	7.2	238	69.0	5.4	0.0107	0.104	17
V <sub>3</sub> Si	16.8	12.6	435	32.5	52.3	0.0030	0.388	9,10
Nb <sub>3</sub> Sn	17.8	13.7	254.3	60.1	33	0.0267	0.228	9,10
Re <sub>3</sub> W	9	8.3	300.1	88.7	16.4	0.0556	0.094	8
MgCNi <sub>3</sub>	6.4	7.5	301.0	77.5	37.4	0.0242	0.097	12
NbSe <sub>2</sub>	7.3	5.4	235.5	49.2	19.3	0.0081	0.110	14,15
Nb <sub>0.8</sub> Ta <sub>0.2</sub> Se <sub>2</sub>	5.1	4.5	219.6	48.0	14.6	0.0048	0.094	14,15
YCo <sub>2</sub> B <sub>2</sub>	0	8.9	575.9	116.2	6.7	0.0091	0.077	17
LaNi <sub>2</sub> B <sub>3</sub> C	0	8.2	443.4	82.1	8.0	0.0098	0.100	17
La(Pt <sub>0.8</sub> Au <sub>0.2</sub> ) <sub>2</sub> B <sub>2</sub> C	10.7	5.6	269.7	54.4	7.1	0.0077	0.103	13
Y(Pt <sub>0.2</sub> Ni <sub>0.8</sub> ) <sub>2</sub> B <sub>2</sub> C	12.1	10	461.7	106.0	14.6	0.0258	0.094	14,15
YNi <sub>2</sub> B <sub>2</sub> C ( <i>sc</i> )	15.4	12.8	481.7	136.8	20.6	0.0410	0.094	14-16
YNi <sub>2</sub> B <sub>2</sub> C ( <i>pc</i> )	14.3	13	463.1	164.0	17.9	0.0709	0.079	13
LuNi <sub>2</sub> B <sub>2</sub> C ( <i>pc</i> )	16.1	10.7	402.3	103.9	19.2	0.0546	0.103	13
LuNi <sub>2</sub> B <sub>2</sub> C ( <i>sc</i> )	16.8	9.2	358.1	95.4	17.6	0.0279	0.096	14,15
Li <sub>2</sub> Pt <sub>3</sub> B	2.56	3.1	231.7	35.4	9.2	0.0380	0.088	17
Li <sub>2</sub> Pd <sub>1.5</sub> Pt <sub>1.5</sub> B	3.9	3.0	242.4	32.2	9.8	0.0030	0.093	17
Li <sub>2</sub> Pd <sub>3</sub> B	6.95	2.0	226.2	28.9	9.4	0.0030	0.069	17

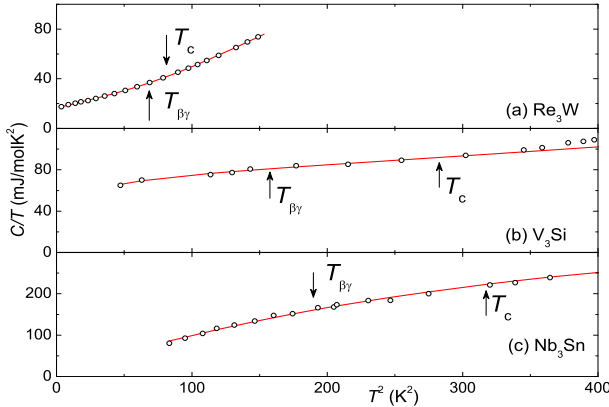


FIG. 2: Isofield  $C/T$  versus  $T^2$  curves of the normal-state of (a)  $\text{Re}_3\text{W}$  at  $H=7$  T,<sup>8</sup> (b)  $\text{V}_3\text{Si}$  at  $H=18$  T,<sup>10</sup> (c)  $\text{Nb}_3\text{Sn}$  at  $H=12.5$  T.<sup>10</sup> Lines are fits to Eq. 8 with parameters as given in Table I. The  $\beta\gamma$ -change of  $\text{Nb}_3\text{Sn}$  and  $\text{V}_3\text{Si}$  is strongly related to the martensitic transformation, which reduces the cubic symmetry of the structure into a low-symmetry one.<sup>10</sup>

the curvature at  $T_{\beta\gamma}$  (see e.g. Figs. 2)].

Second,  $\beta$  and  $\gamma$  are strongly correlated (the electronic and phonic degrees of freedom are strongly coupled) and that the trend of this correlation is not arbitrary: apparently, for the two linearized sections, if  $\gamma_{\text{low}} < \gamma_{\text{high}}$  then  $\beta_{\text{low}} > \beta_{\text{high}}$  and vice versa.

Third, none of the  $C/T$  versus  $T^2$  curves exhibits a discontinuity or a hysteresis effect at  $T_{\beta\gamma}$ .

Fourth, in spite of the above-mentioned differences, there are, at least, two ingredients common to most of the studied materials: a relatively strong electron-phonon coupling and a lifting of spin-degeneracy at  $E_F$ , say, by an applied magnetic field (as in, e.g., conventional superconductors) or by an anisotropic spin orbit coupling ASOC interaction (as in, e.g., non-centrosymmetric  $\text{Li}_2(\text{Pd}_{1-x}\text{Pt}_x)_3\text{B}$  and  $\text{Li}_x\text{RhB}_{1.5}$  superconductors). Curiously, although  $H$  ( $> H_{c2}$ ) is necessary for the quench of the superconductivity and for the lift of spin degeneracy, it has no influence on  $T_{\beta\gamma}$ ,  $\beta$  or  $\gamma$ .<sup>9,10,13-15</sup> Fifth,  $T_{\beta\gamma}$  can be controlled by substitution.

Various investigators attributed this  $\beta\gamma$ -change to an anomaly in the phonon<sup>5,19,20</sup> or electron<sup>5</sup> density of states DOS curves.<sup>5</sup> Attempts were made to supplement the Debye model by assuming either an additional Einstein mode<sup>20</sup> or a variation of the effective  $\theta_D$ :<sup>1</sup> for the latter case, it is often argued that, based on a typical phonon spectrum,  $\theta_D(T)$  must decrease as the thermal energy is raised towards the first peak of the phonon spectrum.<sup>21</sup>

Two investigations deserve a special mention: First, Stewards *et al.*<sup>9,10</sup> attributed the  $\beta\gamma$ -change in  $\text{Nb}_3\text{Sn}$  and  $\text{V}_3\text{Si}$  to the inability of some acoustic phonons to decay through the creation of electron-quasiparticle pairs: the opening of the superconducting gap  $\Delta_s$  leads to an

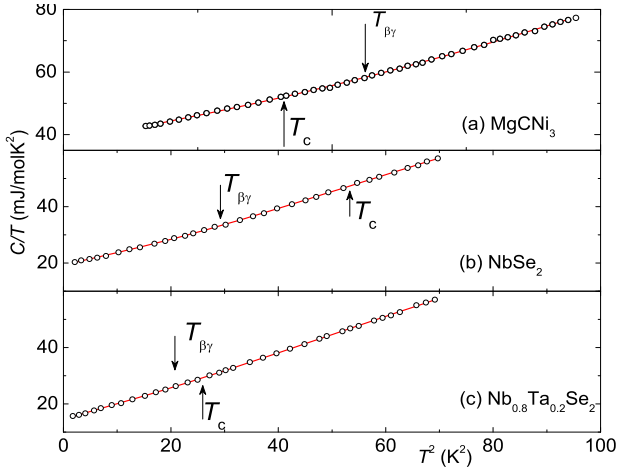


FIG. 3: Isofield  $C/T$  versus  $T^2$  curves of (a)  $\text{MgCNi}_3$  at  $H=8$  T,<sup>12</sup> (b)  $\text{NbSe}_2$  at  $H=6$  T,<sup>15</sup> and (c)  $\text{Nb}_{0.8}\text{Ta}_{0.2}\text{Se}_2$  at  $H=4$  T.<sup>15</sup> Lines are fits to Eq. 8 with parameters as given in Table I.

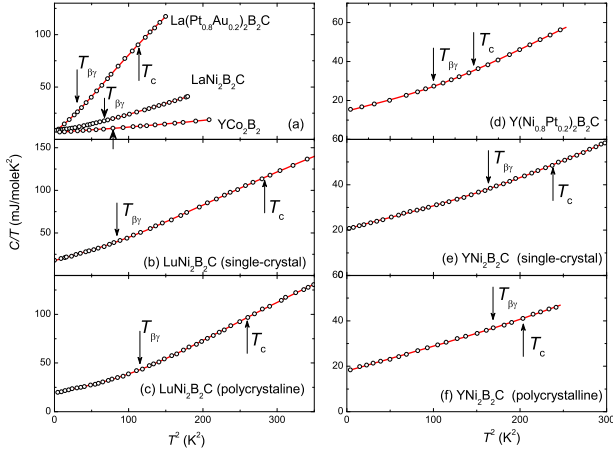


FIG. 4: Isofield  $C/T$  versus  $T^2$  curves of (a)  $\text{La}(\text{Pt}_{0.8}\text{Au}_{0.2})_2\text{B}_2\text{C}$  at  $H=9$  T while  $\text{LaNi}_2\text{B}_2\text{C}$  and  $\text{YCo}_2\text{B}_2$  are at  $H=0$  T,<sup>13</sup> (b) single crystal of  $\text{LuNi}_2\text{B}_2\text{C}$  at  $H=8$  T,<sup>14</sup> (c) polycrystalline  $\text{LuNi}_2\text{B}_2\text{C}$  at  $H=9$  T,<sup>13</sup> (d)  $\text{Y}(\text{Ni}_{0.8}\text{Pt}_{0.2})_2\text{B}_2\text{C}$  at  $H_{\parallel c}=4.5$  T,<sup>15</sup> (e) single-crystal  $\text{YNi}_2\text{B}_2\text{C}$  at  $H_{\parallel c}=12$  T, and (f) polycrystalline  $\text{LuNi}_2\text{B}_2\text{C}$  at  $H=9$  T.<sup>13</sup> Lines are fits to Eq. 8 with parameters as given in Table I.

abrupt change in the lifetimes of phonons with energies less than  $2\Delta_s(T)$ .<sup>9,22</sup> The net results is that  $C_L + C_e$  would be modified. Second, Moore and Paul<sup>19</sup> as well as Leupold *et al.*<sup>5</sup> assumed that the  $\beta\gamma$ -deviation in group V transition metals is related to a Kohn-type anomaly in the phonon (or electron) spectra. They demonstrated that such a deviation can be satisfactorily reproduced if one represents the DOS of such an anomaly by a Dirac delta-function and calculates analytically the total specific heat.

Although these two approaches addressed adequately some features of the  $\beta\gamma$ -deviation, however serious ques-

tions are not fully addressed: e.g. (i) the origin of both  $T_{\beta\gamma}$  and the strong and systematic correlation between  $\beta$  and  $\gamma$ , (ii) the identification of the role played by both the electron-phonon couplings and the dielectric properties of the investigated intermetallics, (iii) the observations that the  $\beta\gamma$ -change occurs in the absence of superconductivity (as in normal intermetallics) and that some superconductors, even with an established  $\Delta_s(T)$ , do not show this  $\beta\gamma$ -change.

In this work, we present a systematic analysis of the above-mentioned anomalous thermal evolution of the specific heat (and resistivity) of various compounds. The dielectric properties of the compounds under study will be taken into consideration. The above-mentioned approaches of Stewards *et al.*<sup>9,10</sup> and Moore and Paul<sup>19</sup> will be partially modified, extended, and generalized. The obtained analytical expression for the total specific heat (electron plus phonon) is shown to reproduce satisfactorily the studied experimental curves.

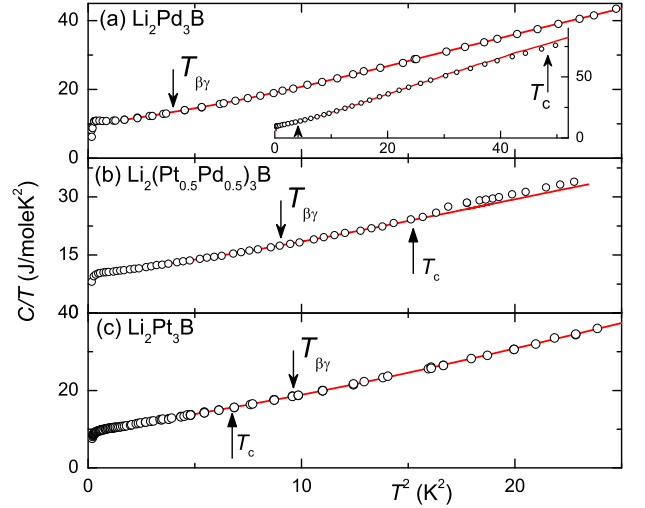


FIG. 5: Isofield  $C/T$  versus  $T^2$  curves of the normal-state of (a)  $\text{Li}_2\text{Pd}_3\text{B}$  at  $H=5$  T, (b)  $\text{Li}_2(\text{Pd}_{0.5}\text{Pt}_{0.5})_3\text{B}$  at  $H=3$  T, and (c)  $\text{Li}_2\text{Pt}_3\text{B}$  at  $H=3$  T.<sup>17</sup> Lines are fits to Eq. 8 with parameters as given in Table I.

## II. THEORETICAL BACKGROUND

### A. Lattice specific heat

An anomaly, such as a Kohn type, in the phonon DOS can be represented, as done in earlier investigations,<sup>5,19</sup> by a Dirac delta function. Then

$$D(E) = a \cdot 3N_L \cdot E^2 + b \cdot 3N_L \cdot \delta(E - E_L) \quad (1)$$

where  $N_L = rN_A$  is the number of total atoms,  $N_A$  is the Avogadro number, and  $E_L = k_B\theta_L$  is the energy at which the Dirac-type anomaly is situated.  $a$  and  $b$  represent the fractional weights and are related by the

normalization condition  $\int_0^{E_D} D(E).dE = 3rN_A$  which gives

---

$a = 3(1 - b)/(k\theta_D)^3$ . The lattice specific heat is then

$$C_L(T) = \int_0^{E_D} E.D(E) \frac{1}{\exp(\frac{E}{k_B T}) - 1} dE = \sum_{n=1}^{\infty} \int_0^{E_D} E.D(E) \cdot \exp(-\frac{nE}{k_B T}) dE = \frac{12}{5} \pi^4 N_L k_B \left(\frac{T}{\theta_D}\right)^3 \xi = \beta_0 T^3 \xi \quad (2)$$

$$\xi = (1 - b) \left\{ 1 - \frac{15}{4\pi^4} \left(\frac{\theta_D}{T}\right)^4 L_0(Z_D) - \frac{15}{\pi^4} \left(\frac{\theta_D}{T}\right)^3 L_1(Z_D) - \frac{45}{\pi^4} \left(\frac{\theta_D}{T}\right)^2 L_2(Z_D) - \frac{90}{\pi^4} \left(\frac{\theta_D}{T}\right) L_3(Z_D) - \frac{90}{\pi^4} L_4(Z_D) \right\} \\ + b \left\{ \frac{5}{4\pi^4} \left(\frac{\theta_D}{T}\right)^3 \left(\frac{\theta_L}{T}\right)^2 L_{-1}(Z_L) \right\} \quad (3)$$


---

where  $L_i(Z)$  is the polylogarithm function;  $Z_D = \exp(-\theta_D/T)$ ;  $Z_L = \exp(-\theta_L/T)$ . The expression with  $b = 0$  is the usual Debye contribution (for numerical calculation, this form is much better than the one given in solid-state text books).<sup>1,21</sup> The Debye  $T^3$  expression is obtained when  $T \rightarrow 0$  [ $\xi$  acts as a  $T$ -dependent correction factor, see Fig. 6(a)] while the Dulong-Petit value is reached when  $T > \theta_D$ . Eq. 2 justifies the often-used procedure of treating the  $\beta\gamma$ -deviation as a thermal variation of an effective temperature-dependent  $\theta'_D = \theta_D/\xi^{1/3}$ : indeed Fig. 6 (b) reproduces the often-observed thermal variation of  $\theta'_D$ .

The low-temperature limit of Eq. 2 reproduces the expressions of Moore and Paul<sup>19</sup> as well as that of Leupold *et al.*<sup>5</sup> Evidently, the introduction of that anomaly leads to both a Debye-type contribution with weight factor  $(1 - b)$  and an Einstein-type contribution with frequency  $\omega_L$  and weight factor  $b$ . The latter conclusion justifies the often-used practice of adding an Einstein contribution to the specific heat of such intermetallic systems.<sup>20</sup>

## B. Electronic specific heat

Along similar lines, a DOS curve of an electron subsystem with an additional Dirac delta function can be

---

represented as<sup>5</sup>

$$N(E) = c.N_E.E^{\frac{1}{2}} - d.N_E.\delta(E - E_E) \quad (4)$$

where  $N_E = xN_A$  is the total number of conduction electrons and  $E_E = k_B\theta_E$  denotes the position of the Dirac-type anomaly.  $c$  and  $d$  are fractional weights that are related by the normalization condition

$$\int_0^{\infty} dE.N(E)/\left(\exp\left(\frac{E - E_F}{k_B T}\right) + 1\right) = xN_A. \quad (5)$$

This gives

$$c \cong \frac{1 + d/[1 + \exp((\theta_E - \theta_F)/T)]}{\frac{2}{3}E_F^{3/2} [1 + (\pi T/\sqrt{8}\theta_F)^2]}.$$

As the electron number is independent of temperature, then the thermal rate of the chemical potential is  $-\pi^2 k_B^2 T/6E_F$  as  $T \rightarrow 0$ .

Using Sommerfeld expansion in the expression of the electronic energy and taking the derivative with respect to temperature, one obtains

$$C_E(T) \cong \frac{\pi^2 N_E k_B T}{2\theta_F} \eta = \gamma_0 T \eta \quad (6)$$

$$\eta = 1 + \frac{d}{1 + \exp((\theta_E - \theta_F)/T)} - d \frac{1}{2\pi^2 T^3} \theta_E \theta_F (\theta_E - \theta_F) \operatorname{sech}^2((\theta_E - \theta_F)/2T) \quad (7)$$


---

$\eta$  is a  $T$ -dependent correction factor, see Fig. 6(c). Eq.6 is a sum of three contributions: the first is the usual Sommerfeld expression ( $d = 0$ ) while the second and third

terms are related to the Dirac delta function.

### C. Total specific heat (Lattice plus electron)

From Eqs. 2 and 6, the total  $C/T$  versus  $T^2$  can be presented in the familiar form

$$C/T = \gamma_0 \eta + \beta_0 \xi T^2 = \gamma + \beta T^2 \quad (8)$$

For  $T < \theta_D \ll \theta_F$ ,  $\theta_E \ll \theta_F$ , and  $\theta_L < \theta_D$ , both linear Sommerfeld and cubic Debye approximation are obtained but with effective  $\gamma$  and  $\beta$ . Fig. 6(d) shows that, within this temperature range, the thermal evolution of  $\eta$  and  $\xi$  (consequently that of  $\gamma$  and  $\beta$ ) leads to the experimentally observed two limiting behaviors. Analytically, the low-temperature ( $\theta_E, \theta_L > T_{\beta\gamma} > T \rightarrow 0$ ) limit is

$$\gamma_{low} = \gamma_0(1 + d) \quad (9)$$

$$\beta_{low} = \beta_0(1 - b) \quad (10)$$

while the high-temperature ( $\theta_E, \theta_L > T > T_{\beta\gamma}$ ) limit is

$$\gamma_{high} \approx \gamma_0 \left[ 1 + d \left( 1 + \frac{4}{\pi^2} \frac{\theta_E}{\theta_F} X^3 \text{sech}^2(-X) \right) \right] \quad (11)$$

$$\frac{\gamma_{high}}{\gamma_{low}} = 1 + \frac{4d\theta_E X^3 \text{sech}^2(-X)}{\pi^2(1 + d)\theta_F} \quad (12)$$

$$\beta_{high} \approx \beta_0 \left[ 1 - b \left( 1 - \frac{5}{4\pi^4} \left( \frac{\theta_D}{\theta_L} \right)^3 \right) \right] \quad (13)$$

$$\frac{\beta_{high}}{\beta_{low}} = 1 + \frac{5b}{4\pi^4(1 - b)} \left( \frac{\theta_D}{\theta_L} \right)^3 \quad (14)$$

where  $X = \theta_F/2T$ . The thermal variation of  $\gamma$  (Eqs. 7, 9, 11) as compared to that of  $\beta$  (Eqs. 3, 10, 13) is extremely small: as a consequence the thermal variation of Eq. 8 is predominantly governed by that of  $\beta$ . This explains the reported success in analyzing the specific heats of group V transition metals in terms of  $C/T = \gamma_{low} + \beta_0 \xi T^2$ .<sup>5,19</sup> Then the intensity and extent of slope break are related mainly to  $\xi$  (Eq. 3) (extremely weak dependence on  $\theta_E$ ,  $N_E$ , and  $d$  is expected). This conclusion allows us to define  $T_{\beta\gamma}$  as the point of inflection in the  $\xi(T)$  curve [see Eq. 3 and Fig. 6(a)]. Then the solution of  $\partial^2 \xi / \partial T^2 = 0$  gives

$$T_{\beta\gamma} = \frac{\theta_L}{5} \left( 1 \pm \frac{1}{\sqrt{6}} \right) \cong 0.12\theta_L, 0.28\theta_L \quad (15)$$

These two calculated ratios of  $\frac{T_{\beta\gamma}}{\theta_L}$  are in reasonable agreement with the experimentally determined values of Nb which manifests two slope breaks:<sup>2-5,19,23</sup> one at  $T'_{\beta\gamma} = 3.11$  K while the other at  $T''_{\beta\gamma} = 10.3$  K. Using  $\theta_L = 31.3$  K (see Table I), then the calculated  $T'_{\beta\gamma} = 3.8$  K while  $T''_{\beta\gamma} = 8.8$  K (the experimental  $\frac{T_{\beta\gamma}}{\theta_L}$  ratios are, respectively, 0.10 and 0.33). It is noted that the high  $T_{\beta\gamma}$ -event (showing the highest discrepancy) was not reported<sup>5</sup> for the isomorphous Ta and V suggesting that it might be unique to Nb.

Equations 13-14 predict a positive curvature and  $\beta_{high} > \beta_{low}$  whenever  $b > 0$ : this is consistent with the features of all analyzed curves in Figs. 1-5 except those of V<sub>3</sub>Si and Nb<sub>3</sub>Sn; these indicate that  $b < 0$ .

The above arguments, in particular Fig. 6, emphasize that, the slope break (whether smooth or sharp) is not a phase transition, rather it is a consequence of the thermal evolution of  $\xi$  (and, to a lesser extent,  $\eta$ ): indeed no thermodynamic phase transition in borocarbides was reported in the extensively measured low- $T$  magnetoresistivity,<sup>24-27</sup> thermopower<sup>27</sup>, thermal conductivity,<sup>28</sup> Hall,<sup>29</sup> and thermal expansion<sup>30</sup> properties.

### D. The correlation of $\theta_D$ ( $\beta$ ) and $\gamma$

A correlation between  $\beta$  and  $\gamma$  can be obtained if we consider the low-temperature specific heat of these intermetallics as being due to Sommerfeld-type electrons and longitudinal acoustic Debye-type phonons. As the total dielectric function (electrons plus ions) of these longitudinal modes must be zero, then the sound velocity, as  $|\vec{k}| \rightarrow 0$ , would be  $v_s = v_F \sqrt{m/3M}$ , where  $v_F$ ,  $m$ , and  $M$  denote, respectively, the Fermi velocity, the electronic mass, and ionic mass.<sup>21</sup> Inserting this  $v_s$  into  $\theta_D$  (as obtained from the Debye model) and replacing  $v_F$  by  $\gamma$  (as obtained from Sommerfeld model) one gets the correlation of  $\gamma$  and  $\theta_D$ :

$$\gamma = \left( \frac{3\pi^4 h^6 N_A^5}{2} \right)^{1/3} \frac{1 + d}{M} \left( \frac{x^3 r^2}{V_m^2} \right)^{1/3} \frac{1}{\theta_D^2} \quad (16)$$

where  $V_m$  is the molar volume. For  $N_E = N_L$  (or  $x = r$ ) and  $\theta_D$  as obtained from Table I, Eq. 16 gives  $\gamma_{cal}$  having the same order of magnitude as the experimentally determined  $\gamma$ .

### E. The $T_{\beta\gamma}$ -event as a resistivity drop

The  $T_{\beta\gamma}$ -events in Nb,<sup>5</sup> Fig. 1, and its Nb<sub>1-x</sub>Y<sub>x</sub> ( $Y = \text{Ti, W}$ ) alloys were confirmed by the manifestation of a resistivity drop, at the same  $T_{\beta\gamma}$ .<sup>31</sup> Based on the above-mentioned arguments, this drop can be interpreted along the following two lines: (i) The electronic concentration  $n$  in the neighborhood of  $T_{\beta\gamma}$  varies as  $n_0/\eta^{3/2}$  ( $n_0$  is the electronic concentration at  $d = 0$ ). Then an increase in  $n$  below  $T_{\beta\gamma}$  would lead to such a resistivity drop. (ii) The temperature-dependent resistivity is usually approximated by the Bloch-Grüneisen expression:<sup>32</sup>

$$\rho(T) - \rho_0 = (4\pi)^2 (\lambda \omega_p^{-2}) \omega_D \left( \frac{2T}{\theta_D} \right)^5 \int_0^{\frac{\theta_D}{2T}} \frac{x^5}{\sinh(x)^2} dx \quad (17)$$

where  $\rho_0$  is the temperature-independent contribution,  $\lambda$  is the electron-phonon coupling, and  $\omega_p$  is the Drude

plasma frequency ( $\omega_p^2 = 4\pi e^2 n/m$ ; factors have their usual meaning). Then an increase in  $\theta_D$  (a drop in  $\beta$ ) below  $T_{\beta\gamma}$  would be manifested as a decrease in the resistivity.

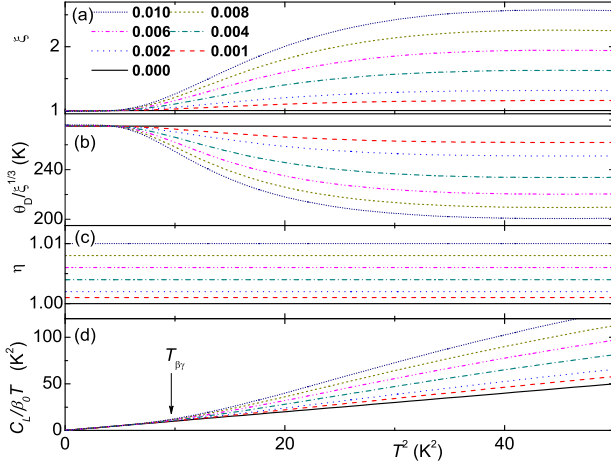


FIG. 6: (Color online) The evolution of (a)  $\xi$ , (b) the effective  $\theta_D' = \theta_D/\xi^{1/3}$ , (c)  $\eta$ , and (d)  $\xi.T^2 = C_L/\beta_0 T$  versus  $T^2$  for various values of  $b$  ( $b = d$ ). The following values were used (typical for Nb):<sup>5</sup>  $\theta_D = 275$  K,  $\theta_L = \theta_E = 33$  K, and  $\gamma_0 = 7.8$  mJ/moleK<sup>2</sup> (see Table I). For  $T < \theta_D$ , the thermal variation of  $\eta$  is almost constant while  $\xi$  varies sharply above  $T_{\beta\gamma}$ . Evidently the slope break at  $T_{\beta\gamma}$  is due to the thermal variation of  $\xi.T^2 = C_L/\beta_0 T = [C_{tot} - \gamma_0(1+d)T]/\beta_0 T$  ( $\beta_0$  and  $\gamma_0$  are  $T$ -independent).

### III. ANALYSIS AND DISCUSSION

All the curves reported in Figs. 1-5 were least-squares analyzed with Eq. 8 assuming  $\theta_E = \theta_L$  and  $d = b$ : these reasonable simplifications would not influence any of the conclusions drawn from this analysis since, as mentioned above, the dominant thermal variation is due to that of  $\xi$ .

As can be observed in Figs. 1-5, there is a satisfactory agreement between theory (solid lines) and experiment (symbol). The fit parameters are shown in Table I: comparison with the published values suggests that the obtained  $\gamma_0$  is as expected but  $\theta_D$  is slightly different: this is attributed to the difference in the criterion for its determination. In addition, Table I shows that (i)  $b$  is extremely small as expected, (ii)  $\gamma_0$  is correlated to  $\theta_D$  through Eq. 16, and (iii) the  $T_{\beta\gamma}/\theta_L$  ratio is in accord with Eq. 15: in fact this ratio can be used to classify the studied compounds: those with  $T_{\beta\gamma}/\theta_L \approx (1 + 1/\sqrt{6})/5$  (such as Nb<sub>3</sub>Sn, V<sub>3</sub>Si) have  $b < 0$  and a negative curvature while all the other with  $T_{\beta\gamma}/\theta_L \approx (1 - 1/\sqrt{6})/5$  have  $b > 0$  and a positive curvature.

Figure 1 shows that  $T_{\beta\gamma} < T_c$  for Nb, while  $T_{\beta\gamma} > T_c$  for Ta and V:<sup>5</sup> thus  $T_{\beta\gamma}$  (or  $\theta_L$ ) is not strictly correlated with the pairing potential. Furthermore  $T_{\beta\gamma}$  does not

show any systematic correlation with the atomic weight: indeed a Kohn-type anomaly is not necessarily related to the atomic masses. Such a nonsystematic feature is evident also in the normal-state curves of the A15 members<sup>10,33</sup> Nb<sub>3</sub>Sn, V<sub>3</sub>Si, and Re<sub>3</sub>W (Fig. 2).

Figure 3 shows a  $\beta\gamma$ -change in MgCNi<sub>3</sub> (with  $T_{\beta\gamma} > T_c$ )<sup>12</sup> as well as in NbSe<sub>2</sub> and Nb<sub>0.8</sub>Ta<sub>0.2</sub>Se<sub>2</sub> ( $T_{\beta\gamma} < T_c$ ).<sup>15</sup> It is noted that a 20% Ta substitution leads to a decrease in  $T_{\beta\gamma}$ . On the other hand, Fig. 4 indicates that  $b$  is reasonably strong for the  $RNi_2B_2C$  compounds indicative of a stronger anomalous contribution. Interestingly, the  $\beta\gamma$ -event is evident also in the nonsuperconductors LaNi<sub>2</sub>B<sub>2</sub>C and YCo<sub>2</sub>B<sub>2</sub>:  $b$  (also  $d$ ) does not depend on the pairing potential. In addition,  $T_{\beta\gamma}$  of  $RNi_2B_2C$  varies over a wider range, from 5 to 13 K even though  $N(E_F)$  does not:<sup>34</sup>  $\theta_L$  does not depend on  $N(E_F)$ . For all  $RNi_2B_2C$ ,  $T_{\beta\gamma}$  ( $< T_c$  when applicable) does manifest a dependence (though unsystematic) on the sample format (single- or poly-crystals) and on the type of isovalent ions  $R^{3+} = Y^{3+}$ ,  $La^{3+}$ ,  $Lu^{3+}$ .

Most of the above-mentioned superconductors are type-II with strong or intermediate-to-strong couplings. Nonetheless, a similar  $\beta\gamma$ -change is evident in non-centro-symmetric superconductors such as Re<sub>3</sub>W (Fig 2(a)),<sup>8,35</sup> Li<sub>2</sub>(Pd<sub>1-x</sub>Pt<sub>x</sub>)<sub>3</sub>B ( $x=0, 0.5, 1$ ) (Fig. 5),<sup>17,36,37</sup> and Li<sub>x</sub>Rh<sub>1.5</sub> ( $x = 0.8, 1.0, 1.2$ ).<sup>18</sup> The space groups of these unconventional superconductors have no inversion symmetry operator and as such there is a relatively strong ASOC interaction which has the effect of lifting the spin-degeneracy at the Fermi surface.<sup>38-41</sup> Then, for, say, Li<sub>2</sub>(Pd<sub>1-x</sub>Pt<sub>x</sub>)<sub>3</sub>B, an increase in  $x$  is accompanied by an increase in the ASOC interaction, in the effectiveness of degeneracy lifting, and in  $T_{\beta\gamma}$ : for lower ASOC,  $T_{\beta\gamma} < T_c$  while for higher ASOC,  $T_{\beta\gamma} > T_c$ .

Equations 12 and 14, each being related to an independent subsystem, suggest an absence of appreciable correlation between  $\left(\frac{\beta_{high}}{\beta_{low}}\right)_{cal}$  and  $\left(\frac{\gamma_{high}}{\gamma_{low}}\right)_{cal}$ : in fact the former depends on  $b$  and  $\frac{\theta_D}{\theta_L}$  while the latter on  $d$ ,  $\frac{\theta_E}{\theta_F}$ , and  $\frac{\theta_F}{T}$ ; only for the  $T \rightarrow 0$  limit,  $\left(\frac{\gamma_{high}}{\gamma_{low}}\right)_{cal}$  is  $T$ -independent but then there is no correlation since it tends to 1. On the other hand, there is a strong correlation between the experimentally determined  $\left(\frac{\beta_{high}}{\beta_{low}}\right)_{exp}$  and  $\left(\frac{\gamma_{high}}{\gamma_{low}}\right)_{exp}$  (obtained from the two linearized sections). This apparent inconsistency can be clarified if we note that (i)  $\beta_{low}$  (Eq. 10) and  $\gamma_{low}$  (Eq. 9) are equal to the experimentally determined ones and both are correlated by Eq. 16, (ii)  $\beta_{high}$  (Eq. 13) is the same as the experimentally determined value but  $\gamma_{high}$  (Eq. 11) is not the same as the experimentally determined value due to the involvement of  $\xi(T)$ : accordingly Eq. 16 can not be used to related the experimentally determined  $\theta_{D,high}$  and  $\gamma_{high}$ .

It seems that for the cases where  $T_{\beta\gamma} < T_c$ , the zero-field superconducting state masks the  $T_{\beta\gamma}$ -event, however, the latter can be recovered if the superconductivity is quenched with, say,  $H > H_{c2}$ . In general, the  $T_{\beta\gamma}$ -event, if dominated by phonon contributions, is



$H$ -independent but can be influenced by substitution. Two type of substitution-induced influences can be identified: in the first, an increase in doping leads to a decrease in  $T_{\beta\gamma}$  such as in the case of  $\text{Y}(\text{Ni}_{1-x}\text{Pt}_x)_2\text{B}_2\text{C}$ ,  $\text{Nb}_{1-x}\text{V}_x$ ,<sup>11</sup> and  $\text{Nb}_{0.8}\text{Ta}_{0.2}\text{Se}_2$ ,<sup>15</sup> while in the second,  $T_{\beta\gamma}$  is increased on doping such as in the case of  $\text{NbW}_x$ ,<sup>4</sup>  $\text{Li}_2(\text{Pd}_{1-x}\text{Pt}_x)_3\text{B}$ ,<sup>17</sup> and  $\text{Li}_x\text{RhB}_{1.5}$ .<sup>18</sup>

Finally, an anomaly in the electron DOS, such as an opening of a pseudogap, would be coupled by a relatively strong electron-phonon interaction to the phonon excitations in the same way as was described above for the case of  $\text{Nb}_3\text{Sn}$ .<sup>10</sup> Similarly, a phonon anomaly would be coupled to the electron excitations.

#### IV. CONCLUSIONS

Variety of compounds exhibit a  $\beta\gamma$ -change; some are conventional type-II superconductors, some are unconventional superconductors, while others are normal intermetallics. In cases where both superconductivity and  $\beta\gamma$ -anomalies are manifested, some compounds exhibit  $T_{\beta\gamma} < T_c$  while others  $T_{\beta\gamma} > T_c$ . The onset of  $\beta\gamma$ -change can be sharp or smooth depending on material properties however such an event is not related to a thermodynamic phase transition. The strength, character, and trend of this  $\beta\gamma$ -change vary widely, nonetheless, there is a systematic correlation between  $\gamma$  and  $\beta$ . Furthermore, this  $\beta\gamma$ -change can be influenced by perturbations such

as ASOC interaction and substitution but hardly by a variation in  $N(E_F)$  or a magnetic field.

It was shown that this  $\beta\gamma$ -change is related to anomalies within the phonon or electron dispersion relation. Assuming a Dirac-type anomaly in the phonon and electron DOS curves, an analytical expression for the thermal evolution of the total specific heat of the electron and phonon quasiparticles was derived and was found to compare favorably with the studied experimental curves. The term expressing the lattice contribution can be interpreted either as a sum of a Debye and an Einstein mode or else as a Debye term with an effective  $T$ -dependent  $\theta_D$ . The overall features of the resulting  $C/T$  versus  $T^2$  curve indicate (i) a manifestation of a break in the slope at  $T_{\beta\gamma} = 0.2(1 \pm 1/\sqrt{6})\theta_L$ , (ii) that the slope break is mostly determined by the phonon anomaly. The correlation between  $\theta_D$  and  $\gamma$  is traced down to the influence of the dielectric properties on the sound velocity of the low-temperature acoustic phonons. Finally, the drop in the resistivity curve at  $T_{\beta\gamma}$  is shown to be caused by the same mechanism that gives rise to the slope break in the  $C/T$  versus  $T^2$  curve.

#### Acknowledgments

We acknowledge the partial financial support from the Brazilian agency CNPq.

- 
- <sup>1</sup> E. S. R. Gopal, *Specific Heat at Low Temperatures* (Plenum Press, New York, 1966).
  - <sup>2</sup> F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).
  - <sup>3</sup> B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. **134**, A1320 (1964).
  - <sup>4</sup> J. F. da Silva, E. A. Burgemeister, and Z. Dokoupil, Physica **41**, 41 (1969).
  - <sup>5</sup> H. A. Leupold, G. J. Iafrate, F. Rothwarf, J. T. Breslin, D. Edmiston, and T. R. AuCoin, J Low Temp Physics **28**, 241 (1977).
  - <sup>6</sup> N. E. Alekseevskii, G. Wolf, C. Hohlfield, and N. M. Dobrovolskii, J Low Temp. Phys. **40**, 479 (1980).
  - <sup>7</sup> N. Kobayashi, S. Higuchi, and Y. Muto, in *Superconductivity in d- and f- band Metals*, edited by W. Büchel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 173.
  - <sup>8</sup> J. Yan, L. Shan, Q. Luo, W.-H. Wang, , and H.-H. Wen, Chin. Phys. B **18**, 704 (2009).
  - <sup>9</sup> G. R. Stewart, B. Cort, and G. W. Webb, Phys. Rev. B **24**, 3841 (1981).
  - <sup>10</sup> G. R. Stewart and B. L. Brandt, Phys. Rev. B **29**, 3908 (1984).
  - <sup>11</sup> M. Ishikawa and E. Toth, Phys. Rev. B **3**, 1856 (1971).
  - <sup>12</sup> J.-Y. Lin, P. L. Ho, H. L. Huang, P. H. Lin, Y.-L. Zhang, R.-C. Yu, C.-Q. Jin, and H. D. Yang, Phys. Rev. B **67**, 052501 (2003).
  - <sup>13</sup> H. Michor, T. Holubar, C. Dusek, and G. Hilscher, Phys. Rev. B **52**, 16165 (1995).
  - <sup>14</sup> M. Nohara, M. Isshiki, H. Takagi, and R. J. Cava, J. Phys. Soc. Jpn. **66**, 1888 (1997).
  - <sup>15</sup> M. Nohara, M. Isshiki, F. Sakai, and H. Takagi, J. Phys. Soc. Jpn. **68**, 1078 (1999).
  - <sup>16</sup> M. El Massalami, R. E. Rapp, and H. Takeya, in *Studies in High Temperature Superconductors*, edited by A. Narlikar (Nova Science, New York, 2003), vol. 45, p. 153.
  - <sup>17</sup> H. Takeya, M. ElMassalami, S. Kasahara, and K. Hirata, Phys. Rev. B **76**, 104506 (2007).
  - <sup>18</sup> H. Takeya, H. Fujii, M. ElMassalami, F. Chaves, S. Ooi, T. Mochiku, Y. Takano, K. Hirata, and K. Togano, J. Phys. Soc. Jpn. **80**, 013702 (2011).
  - <sup>19</sup> M. A. Moore and D. I. Paul, Solid State Communications **9**, 1303 (1971).
  - <sup>20</sup> W. Pickett and B. Klein, in *Superconductivity in d- and f- band Metals*, edited by W. Büchel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 97.
  - <sup>21</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons Inc., New York, 1996), 7th ed.
  - <sup>22</sup> J. D. Axe and G. Shirane, Phys. Rev. Lett. **30**, 214 (1973).
  - <sup>23</sup> C. Chou, D. White, and H. L. Johnston, Phys. Rev. **109**, 788 (1958).
  - <sup>24</sup> S. Miyamoto, H. Takeya, and Kadowaki, Solid State Commun. **103**, 5 (1997).
  - <sup>25</sup> R. K. Chu, W. K. Chu, Q. Chen, Z. H. Zhang, and J. J H Miller, J. Phys.: Condens. Matter **12**, 275 (200).
  - <sup>26</sup> I. R. Fisher, J. R. Cooper, and P. C. Canfield, Phys. Rev. B **56**, 10820 (1997).

- <sup>27</sup> K. D. Ranthnayaka, A. K. Bhatnagar, A. Parasiris, D. G. Naugle, P. C. Canfield, and B. K. Cho, Phys. Rev. B **55**, 8506 (1997).
- <sup>28</sup> S. Cao, K. Nishimura, and K. Mori, Physica C **341-348**, 751 (2000).
- <sup>29</sup> V. N. Narozhnyi, J. Freudenberger, V. N. Kochetkov, K. A. Nenkov, G. Fuchs, A. Handstein, and K.-H. Müller, Phys. Rev. B **59**, 14762 (1999).
- <sup>30</sup> S. L. Budko, G. M. Schmiedeshoff, G. Lapertot, and P. C. Canfield, J. Phys.: Condens. Matter **18**, 8353 (2006).
- <sup>31</sup> V. Chopra, J. Low Temp Phys **9**, 1 (1972).
- <sup>32</sup> P. B. Allen, in *Quantum Theory of Real Materials*, edited by J. R. Chelikowsky and S. G. Louie (Kluwer, Boston, 1996), p. 319.
- <sup>33</sup> V. Guritanu, W. Goldacker, F. Bouquet, Y. Wang, R. Lortz, G. Goll, and A. Junod, Phys. Rev. B **70**, 184526 (2004).
- <sup>34</sup> K.-H. Müller and V. N. Narozhnyi, Rep. Prog. Phys. **64**, 943 (2001).
- <sup>35</sup> Y. L. Zuev, V. A. Kuznetsova, R. Prozorov, M. D. Van-  
nette, M. V. Lobanov, D. K. Christen, and J. R. Thomp-  
son, Phys. Rev. B **76**, 132508 (2007).
- <sup>36</sup> H. Q. Yuan, D. F. Agterberg, N. Hayashi, P. Badica,  
D. Vandervelde, K. Togano, M. Sigrist, and M. B. Sala-  
mon, Phys. Rev. Lett. **97**, 017006 (2006).
- <sup>37</sup> M. Nishiyama, Y. Inada, and G.-Q. Zheng, Phys. Rev.  
Lett. **98**, 047002 (2007).
- <sup>38</sup> M. Sigrist and K. Ueda, Rev. Mod. Phys. **63**, 239 (1991).
- <sup>39</sup> E. Bauer, I. Bonalde, and M. Sigrist, Low Temp. Phys. **31**,  
748 (2005).
- <sup>40</sup> M. Sigrist, D. F. Agterberg, P. A. Frigeri, N. Hayashi, R. P.  
Kaur, A. Koga, I. Milat, K. Wakabayashia, and Y. Yanase,  
J.M.M.M. **310**, 536 (2007).
- <sup>41</sup> P. A. Frigeri, D. F. Agterberg, and M. Sigrist, New J. Phys  
**6**, 115 (2004).